

# Genuine Active Species Generated from Fe<sub>3</sub>N Nanotube by Synergistic CoNi Doping for Boosted Oxygen Evolution Catalysis

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The surface reconstruction of oxygen evolution reaction (OER) catalysts has been proven favorable for enhancing its catalytic activity. However, what is the active site and how to promote the active species generation remain unclear and are still under debate. Here, the in situ synthesis of CoNi incorporated Fe<sub>3</sub>N nanotubes (CoNi-Fe<sub>3</sub>N) on the iron foil through the anodization/electrodeposition/nitridation process for use of boosted OER catalysis is reported. The synergistic CoNi doping induces the lattice expansion and up shifts the d-band center of Fe<sub>3</sub>N, which enhances the adsorption of hydroxyl groups from electrolyte during the OER catalysis, facilitating the generation of active CoNi-FeOOH on the Fe<sub>3</sub>N nanotube surface. As a result of this OER-conditioned surface reconstruction, the optimized catalyst requires an overpotential of only 285 mV at a current density of 10 mA cm<sup>-2</sup> with a Tafel slope of 34 mV dec<sup>-1</sup>, outperforming commercial RuO<sub>2</sub> catalysts. Density functional theory (DFT) calculations further reveal that the Ni site in CoNi-FeOOH modulates the adsorption of OER intermediates and delivers a lower overpotential than those from Fe and Co sites, serving as the optimal active site for excellent OER performance.

#### batteries and so on. Despite its vital importance, OER is often hampered by its sluggish kinetics due to the complex four-step proton-coupled electron transfer reactions.<sup>[1,2]</sup> Currently, IrO<sub>2</sub> and RuO<sub>2</sub> are benchmark OER catalysts with superior catalytic activity; nevertheless, the high cost and scarcity severely limit their large-scale application. Thus, first-row (3d) transition-metal (Fe, Co, Ni) based compounds<sup>[3-5]</sup> have recently been developed as efficient OER catalysts. Moreover, during OER catalysis, such catalysts can undergo a self-reconstruction towards oxyhydroxides, hydroxides, or oxides (denoted as (oxyhydr)oxides) at the catalyst surface, which are extensively highlighted as the active species,<sup>[6]</sup> further promoting the OER electrocatalysis. Compared with directly prepared (oxyhydr)oxides, the reconstruction-derived counterparts possess more oxygen vacancies, which can tune the surface-oxygen interaction and

# 1. Introduction

Electrocatalytic oxygen evolution reaction (OER) is an essential half reaction of hydrogen–oxygen electrolysis, metal–air

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promote a higher electrocatalysis activity.<sup>[7]</sup> Importantly, the postreconstruction structure usually displays integrating features of the pristine catalyst and in situ generated (oxyhydr)oxides, synergistically boosting the catalytic activity.<sup>[8]</sup> In this regard,

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triggering surface self-reconstruction toward (oxyhydr)oxides is crucial to guarantee the high OER activity of transitionmetal catalysts. Nevertheless, the slow reconstruction kinetics and consequent low degree formation of active (oxyhydr)oxides species inevitably hamper the catalytic activity.<sup>[9,10]</sup> Moreover, due to the complexity of the OER process with more than one intermediates (\*OH, \*OOH, and \*O),<sup>[11]</sup> the detailed information of the reconstructed species, including their crystalline states (amorphous<sup>[10]</sup> or crystalline<sup>[3]</sup>) and the components (oxides,<sup>[12]</sup> hydroxides,<sup>[5]</sup> or oxyhydroxide,<sup>[13]</sup> is still obscure. Therefore, identifying the genuine species of reconstructionderived structure, and further tuning the kinetics to facilitate the reconstruction are imperative for unveiling reaction mechanism and improving the catalytic activity.

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Interstitial iron nitride (E-Fe<sub>3</sub>N), possesses metallic characteristics with continuous Fe6 octahedral structure, has been showing great potential in OER catalysis.<sup>[14-16]</sup> Intriguingly, all Fe atoms in Fe<sub>3</sub>N are nominally in monovalent state (Fe(I)) and coordinated with two neighboring N atoms; this uniform coordination environment makes Fe<sub>3</sub>N an ideal model to identify the active state.<sup>[17]</sup> However, the catalytic activity of pristine Fe<sub>3</sub>N is low largely due to the stable octahedral feature of Fe<sub>3</sub>N and therefore induces the difficulty of the structure reconstruction.<sup>[18]</sup> Experimentally, reconstruction of OER catalyst towards (oxyhydr)oxides can be achieved by the interaction between positively charged metallic atoms at the catalyst surface and OH<sup>-</sup> in electrolyte during the OER process.<sup>[7]</sup> Doping of foreign atoms provides an effective way to introduce the atomic distortion into the catalyst structure and enhance the catalyst surface interaction with the electrolyte, therefore promoting the surface reconstruction and ultimately the catalytic performance.<sup>[19,20]</sup> Considering the close position of Ni and Co to Fe in the periodic table and their similar atomic structure, doping Co/Ni into Fe based catalysts is proved to be a feasible way to manipulate the surface electronic structure and provide more electrocatalytic active sites.<sup>[21,22]</sup> Moreover, to provide more potential active sites, 1D structures, especially nanotubes (NTs),<sup>[23]</sup> are promoted as both interior and exterior surfaces of these nanostructures can be utilized for catalysis.

Herein, we report the in situ synthesis of CoNi co-doped Fe<sub>3</sub>N (CoNi-Fe<sub>3</sub>N) NTs on the iron foil through the anodization/electrodeposition/nitridation process for highperformance OER catalysis. CoNi co-doping induces up-shift d-band center and render lattice expansion in CoNi-Fe<sub>3</sub>N, which facilitates the OH adsorption and promotes the catalyst surface reconstruction during the OER process. Through various in situ characterization techniques, we find that under OER conditions, all three trimetallic sites, Ni, Co, and Fe, participate in the phase transformation, where the surface of CoNi-Fe<sub>3</sub>N NTs reconstructs into crystalline CoNi-FeOOH via CoNi-Fe(OH)<sub>3</sub> intermediates. Due to this surface reconstruction, massive active sites are generated accounting for the enhanced OER catalytic performance, including an overpotential of only 285 mV at a current density of 10 mA cm<sup>-2</sup> with a Tafel slope of 34 mV dec<sup>-1</sup>. Further density functional theory (DFT) calculations reveal that in CoNi-FeOOH, the Ni site offers near-optimal energetics for all OER intermediates, resulting in a lower overpotential than those of Co- and Ni- single doped counterpart, consistent with our experimental

results. Our findings here not only provide fundamental insight about the catalytic mechanism in  $Fe_3N$  based catalyst materials, but also shed light in their practical use in future energy conversion and storage applications.

## 2. Results and Discussion

#### 2.1. CoNi-Fe<sub>3</sub>N NTs

A series of Fe<sub>3</sub>N based NTs with Co and Ni doping were synthesized on the iron foil by a three-step process (Figure 1a). Firstly, the iron foil was electrochemically anodized into self-organized iron oxide (FeO<sub>v</sub>) NTs, as described in our previous study.<sup>[24]</sup> Then, Co and Ni with various proportions were introduced into FeO<sub>v</sub> by co-electrodepositing, yielding amorphous CoNi-FeO<sub>v</sub>. Finally, the CoNi-FeO<sub>v</sub> NTs were converted to CoNi-Fe<sub>3</sub>N NTs with thermal treatment in the NH<sub>3</sub> flow (Figure S1, Supporting Information). The obtained NTs were then directly used as catalysts for OER in alkaline electrolyte. Under OER conditions, vertically aligned CoNi-Fe<sub>3</sub>N NTs would undergo a surface reconstruction towards CoNi-FeOOH through adsorbing OH- ions driven by anodic potential, as schematically shown in Figure 1b. As a result, metallic CoNi-Fe<sub>3</sub>N NTs with active CoNi-FeOOH on surface exhibit efficient and stable OER catalytic activity. For comparison, single metal doped Fe<sub>3</sub>N (Co-Fe<sub>3</sub>N and Ni-Fe<sub>3</sub>N) as well as bare Fe<sub>v</sub>N (without doping) NTs were also prepared. More details are described in the Experiment Section.

The morphology and structure of the as-prepared CoNi-Fe<sub>3</sub>N NTs were investigated with scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD). As displayed in Figure 2a, vertically aligned CoNi-Fe<sub>3</sub>N NTs comprise a film with a thickness of about 1.9  $\mu$ m, which is rich in mesopores with size ranging from 20 to 40 nm (Figure 2b). These well-ordered CoNi-Fe<sub>3</sub>N NTs are vertically aligned, and possess rough wall with a diameter of  $\approx$ 50 nm, forming a 3D NT arrays architecture (Figure 2c). The high-resolution TEM (HRTEM) observations reveal that the wall of CoNi-Fe<sub>3</sub>N NTs is composed of interconnected nanoparticles with abundant grain boundaries, which would provide abundant favorable channels for electrolyte permeation (Figure 2d). On the other hand, pure Fe<sub>v</sub>N NTs tend to aggregate together (Figure S2, Supporting Information), indicating that doping of CoNi can stabilize the 1D NT structure. As for the single-metal doped samples, Co-Fe<sub>3</sub>N and Ni-Fe<sub>3</sub>N NTs clearly show overgrowths, which block the open pores of NTs (Figure S3, Supporting Information). These distinct morphologies are ascribed to the unique in situ electrodepositing behavior of Co and Ni (Figure S4, Supporting Information),<sup>[25]</sup> implying that the synergistic interactions among all three metals are essential to the uniform distribution of dopants and regular NTs.

To investigate the atomic arrangement of CoNi–Fe<sub>3</sub>N, highangle annular dark-field scanning TEM (HAADF–STEM) was conducted. As illustrated in Figure 2e, HAADF–STEM image of an individual CoNi–Fe<sub>3</sub>N NT coupled with its energy-dispersive X-ray spectroscopy (EDS) elemental mapping result exhibits homogeneous distribution of Co, Ni, Fe, and N elements





Figure 1. Schematic illustration. a) Synthetic route of CoNi–Fe<sub>3</sub>N NTs. b) The surface reconstruction of CoNi–Fe<sub>3</sub>N NTs during OER catalysis.

throughout the whole NT. The selected area electron diffraction pattern (SAED, Figure S5, Supporting Information) further manifests the crystalline structure of Fe<sub>3</sub>N (hcp, PDF#72-2125) in CoNi-Fe<sub>3</sub>N NT. Furthermore, the doping level can be easily tuned by changing the doping ratio of Co to Ni during the growth of CoNi-FeO<sub>v</sub> precursor nanotube arrays. According to the inductively coupled plasma mass spectrometry (ICP-MS) analysis (Table S1, Supporting Information), the proportion of Co and Ni dopants in CoNi-Fe<sub>3</sub>N is 7.17 wt%, two times higher than that of Co-Fe<sub>3</sub>N (2.13 wt%) and Ni-Fe<sub>3</sub>N (3.02 wt%), validating that co-electrodepositing favors an increased doping content. Aberration-corrected HAADF-STEM imaging of CoNi-Fe<sub>3</sub>N also confirms the crystalline nature of Fe<sub>3</sub>N (Figure 2f), and the corresponding Z-contrast image further illustrates the lattice defect with Fe atom vacancies ( $V_{\rm Fe}$ ), which are denoted by the dash circles. Figure 2g shows the XRD patterns of Co-Fe<sub>3</sub>N, Ni-Fe<sub>3</sub>N, CoNi-Fe<sub>3</sub>N, and Fe<sub>v</sub>N. CoNi-Fe<sub>3</sub>N exhibits the characteristic peaks for Fe<sub>3</sub>N, accordant with SAED pattern (Figure S5, Supporting Information). There are no XRD peaks belonging to crystalline cobalt nitrides or nickel nitrides, validating that Co and Ni atoms diffuse into the Fe<sub>3</sub>N lattice. Additionally, because Fe, Co, and Ni are adjacent to each other in the periodic table with similar atomic radius and mass, they are apt to form a solid solution phase or substitute with each other, and Co(Ni)Fe<sub>2</sub>O<sub>4</sub> is formed on the internal wall of NT with a floating content of Fe and doped Co(Ni). [26,27] Notably, compared with Fe<sub>v</sub>N, the (110), (002), (111), and (112) peaks of Fe<sub>3</sub>N in CoNi-Fe<sub>3</sub>N shift to lower angles (right of Figure 2g and Figure S6, Supporting Information), indicating the lattice expansion after Co and Ni doping, which enlarges the atomic Fe-N/Fe bonds and weakens atomic interactions.<sup>[28]</sup>

To further analyze chemical composition and the valence states of  $Fe_3N$  based NTs, X-ray photoelectron spectroscopy

(XPS) was carried out. As displayed in Figure 2h and S7, Supporting Information, the Fe 2p spectra can be divided into two regions representing Fe  $2p_{3/2}$  and Fe  $2p_{1/2}$ , each of which is further deconvoluted into oxidized Fe  $^{\delta+}$  (Fe<sup>2+</sup> and Fe<sup>3+</sup>) from Fe-N/O bonds and metallic Fe<sup>0</sup> from Fe-Fe bonds.<sup>[29]</sup> The binding energy of  $Fe^{\delta+}$  from Co-Fe<sub>3</sub>N, Ni-Fe<sub>3</sub>N, and CoNi-Fe<sub>3</sub>N shifts negatively by 0.3 eV compared with that of pristine Fe<sub>v</sub>N, indicating the electron transfer from Co and Ni to Fe.<sup>[30]</sup> With dual metal co-doping, the Co<sup> $\delta$ +</sup> (Co<sup>2+</sup> and Co<sup>3+</sup>) and Ni<sup> $\delta$ +</sup> (Ni<sup>2+</sup> and Ni<sup>3+</sup>) peaks in CoNi–Fe<sub>3</sub>N are shifted to lower and higher binding energy, respectively, when compared to that in Co-Fe<sub>3</sub>N and Ni-Fe<sub>3</sub>N (Figure S8, Supporting Information, manifesting a coupled charge redistribution among Co, Ni, and Fe. Similarly, the N-Fe peak from CoNi-Fe<sub>3</sub>N shifts negatively by 0.16 eV after CoNi incorporation when compared with that of Fe<sub>v</sub>N (Figure S9, Supporting Information). Also, a new N-Co(Ni) peak appears at around 399.3 eV in the XPS spectrum of CoNi-Fe<sub>3</sub>N, which demonstrates generated amorphous Co-N and Ni-N species and implies an electron donation from Co and Ni to N due to the high electronegativity of N.<sup>[31,32]</sup> In this way, CoNi co-doping effectively weakens the electron-withdrawing from Fe to N, enabling more electron accumulation at Fe, which decreases the Fe-N bond strength and therefore improves the structure distortion. Additionally, in the XPS O 1s spectrum of CoNi-Fe<sub>3</sub>N (Figure 2i), subpeak of oxygen vacancy ( $V_0$ ) at about 530.5 eV enhances when compared with that of Fe<sub>v</sub>N, which is attributed to the Ni(Co)-O bond formation during electrodeposition as well as the M-O (M = Fe, Co, Ni) bond breaking during nitridation (Figure S10, Supporting Information).<sup>[33]</sup> Notably, CoNi-Fe<sub>3</sub>N presents an enhanced O-H signal than that of Fe<sub>v</sub>N, indicating a hydroxy-terminated surface. As a result, an improved hydrophilic nature is

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Figure 2. Characterizations of CoNi-Fe<sub>3</sub>N NTs. a) Cross-section and b) top-view SEM images of CoNi-Fe<sub>3</sub>N NTs. c,d) TEM and e) HAADF-STEM images and corresponding EDS elemental mappings of CoNi-Fe<sub>3</sub>N NTs. f) Aberration-corrected atomic resolution HAADF-STEM image of CoNi-Fe<sub>3</sub>N NTs (top), and the intensity profile along superimposed square (bottom). g) XRD patterns (left) and the enlarged XRD patterns of (111) planes (right) from CoNi-Fe<sub>3</sub>N, Co-Fe<sub>3</sub>N, Ni-Fe<sub>3</sub>N, and Fe<sub>9</sub>N NTs. XPS spectra of h) Fe 2p and i) O 1s from CoNi-Fe<sub>3</sub>N and Fe<sub>9</sub>N. Insert of (i): water CA of the corresponding NTs.

observed in CoNi-Fe<sub>3</sub>N with a smaller water contact angle (CA) (9.8°) than that in  $Fe_{\nu}N$  (14.8°) (insert of Figure 2i). Furthermore, CoNi-Fe<sub>3</sub>N demonstrates a large air bubble CA of 152.3°, indicating an underwater superaerophobic

surface (Figure S11, Supporting Information). The hydrophilic and aerophobic feature of CoNi-Fe<sub>3</sub>N endows a facile mass transfer of hydroxyl ion and gas dissipation, which is beneficial for the solid-liquid-gas OER electrocatalysis.

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#### 2.2. Evaluation of Electrocatalytic Activity

OER electrocatalytic activities of CoNi–Fe<sub>3</sub>N NTs were evaluated in 1.0 mmm KOH solution using a standard three-electrode configuration. For comparison, Co–Fe<sub>3</sub>N, Ni–Fe<sub>3</sub>N, Fe<sub>y</sub>N, CoNi–FeO<sub>y</sub>, and commercial RuO<sub>2</sub> were also tested. As displayed in linear sweep voltammetry (LSV) curves (**Figure 3**a and S12, Supporting Information), CoNi–Fe<sub>3</sub>N delivers remarkable catalytic activity with onset potential ( $\eta_{onset}$ ) of 70 mV, and overpotential of 285 mV to drive 10 mA cm<sup>-2</sup> ( $\eta_{10}$ ), which are lower than those of Ni–Fe<sub>3</sub>N (245, 299 mV), Co–Fe<sub>3</sub>N (278, 317 mV), and Fe<sub>y</sub>N (334, 401 mV), even surpassing benchmark RuO<sub>2</sub> (248, 342 mV), respectively. The reaction kinetics of catalyst was further analyzed based on corresponding Tafel slopes. OER is initiated by the OH<sup>-</sup> adsorption on the active site (\*) based on a four-electron mechanism,<sup>[34]</sup> as shown in Equations (1)–(4)

$$OH^- + * \rightarrow *OH + e^-$$

$$*OH + OH^{-} \rightarrow *O + H_2O + e^{-}$$
<sup>(2)</sup>

$$*O + OH^{-} \rightarrow *OOH + e^{-}$$
(3)

$$*OOH + OH^{-} \rightarrow O_2 + H_2O + e^{-}$$
<sup>(4)</sup>

Generally, when the OH<sup>-</sup> adsorption on active sites (Equation (1)) is the rate-determining step (RDS), the Tafel slope would be  $\approx$ 120 mV dec<sup>-1</sup>. If the deprotonation of \*OH towards \*O (Equation (2)) is the RDS, the Tafel slope would be  $\approx$ 40 mV dec<sup>-1</sup>.<sup>[35,36]</sup> In our case, CoNi–Fe<sub>3</sub>N, Ni–Fe<sub>3</sub>N, Co–Fe<sub>3</sub>N and Fe<sub>y</sub>N, respectively exhibit Tafel slopes of 34.0, 39.5, 39.0, and 38.8 mV dec<sup>-1</sup> (Figure 3b), indicating that the \*O formation with Equation (2) is the RDS. Moreover, Tafel slopes of these Fe<sub>3</sub>N based catalysts are much lower than that of RuO<sub>2</sub> (64.0 mV dec<sup>-1</sup>), demonstrating a favorable kinetics. The low values of Tafel slope and  $\eta_{10}$  indicate that CoNi–Fe<sub>3</sub>N is among the rank of excellent iron-containing OER catalysts (Table S2, Supporting Information).



(1)

**Figure 3.** OER catalytic performances of  $Fe_3N$  based NTs. a) LSV plots, b) corresponding Tafel slopes, c) TOF values and d) CV of  $Fe_3N$  based NTs. e) Nyquist plot and the curves fitted by the electrical equivalent circuit (inset) for  $CoNi-Fe_3N$  and  $Fe_\gamma N$  NTs. f) Surface coverage of OER intermediates of  $CoNi-Fe_3N$  and  $Fe_\gamma N$  NTs. g) Multi-current step test for  $CoNi-Fe_3N$  NTs, (left inset: the polarization curves before and after 1000 LSV cycles; right inset: the enlargement of the area denoted by the dashed circle).



The intrinsic OER catalytic activity is also evaluated by calculating turnover frequency (TOF) at each active site (Figure S13, Supporting Information). CoNi-Fe<sub>3</sub>N delivers a high TOF of 8.9 s<sup>-1</sup> at the overpotential of 300 mV (Figure 3c), which is 2.3, 9.4, 73.0, and 5.0 times higher than that of Ni-Fe<sub>3</sub>N, Co-Fe<sub>3</sub>N, Fe<sub>v</sub>N, and RuO<sub>2</sub>, respectively, verifying enhanced catalytic activity. From the cyclic voltammetry (CV) plots of OER-conditioned NTs (Figure 3d), Fe<sub>v</sub>N presents no precatalytic redox feature in the potential window, while Ni-Fe<sub>3</sub>N and Co-Fe<sub>3</sub>N display sharp redox waves assigned to Ni and Co reversible reactions, respectively, between 2+ and 3+ oxidation states.<sup>[37]</sup> Thus, the voltammetry of CoNi-Fe<sub>2</sub>N is characterized by two types of primary features: one for the Co and Ni redox couples and the other for the oxygen evolution. As compared to Co-Fe<sub>3</sub>N and Ni-Fe<sub>3</sub>N, the integrated peak area of CoNi-Fe<sub>3</sub>N enlarges accordingly, indicating boosted catalytic activity.

Furthermore, in situ electrochemical impedance spectroscopy (EIS) analyses were conducted to inspect the reaction behaviors (Figure S14, Supporting Information). The Nyquist plots were fitted by the equivalent circuit model shown in Figure 3e inset and Figure S15 in the Supporting Information. The uncompensated series resistance, an intercept with the real axis, is abbreviated as  $R_s$ . While the subsequent small arc and semicircle reflect the charge transfer resistance  $(R_{ct})$ .<sup>[38]</sup> In detail, at higher frequency region, the small arc was fitted with a resistance ( $R_1$ ) and double layer capacitance ( $C_{dl}$ ); whereas, at medium to lower frequency region, the semicircle was fitted with a resistance  $(R_2)$  coupled with the capacitance of intermediate adsorption ( $C_{ads}$ ), which signify the adsorption–desorption kinetics of the electrode materials.<sup>[39,40]</sup> All NTs catalysts exhibit small  $R_s$  of  $\approx 10 \Omega$ , demonstrating small parasitic ohmic loss of self-supported electrode architecture. While the subsequent  $R_{\rm ct}$  $(R_1 + R_2)$  of Fe<sub>v</sub>N (1929  $\Omega$ ) is notably reduced to 10.76  $\Omega$  after CoNi incorporation. The extremely decreased R<sub>ct</sub> of CoNi–Fe<sub>3</sub>N indicates that CoNi doping induced porous nanotube arrays can favor the formation of ohmic contact at the catalyst-electrolyte interface and facilitate the adsorption-desorption in catalyst layer, even improve the charge-transfer ability to accelerate the kinetics for the oxygen evolution. By integrating the  $C_{ads}$  with increasing applied potential (E), surface coverage of intermediates ( $\theta$ ) during reaction can be estimated according to equation<sup>[40,41]</sup>

$$C_{\rm ads}(E) = \sigma(d\theta(E) / dE)$$
(5)

where  $\sigma$  is the charge density for monolayer coverage, and assumed to be constant. As exhibited in Figure 3f and Figure S16 in the Supporting Information, CoNi–Fe<sub>3</sub>N demonstrates a larger  $\theta$  than Fe<sub>y</sub>N, suggesting a stronger intermediate adsorption per active site.<sup>[42]</sup> Furthermore, double layer capacitance ( $C_{dl}$ ) was probed to estimate the electrochemical surface area (ECSA) of the catalyst (Figure S17, Supporting Information). Impressively, the  $C_{dl}$  and ECSA values of CoNi– Fe<sub>3</sub>N (7.70 mF cm<sup>-2</sup>, 192.5 cm<sup>2</sup>) are much higher than those of Ni–Fe<sub>3</sub>N (2.10 mF cm<sup>-2</sup>, 52.5 cm<sup>2</sup>), Co–Fe<sub>3</sub>N (1.38 mF cm<sup>-2</sup>, 34.5 cm<sup>2</sup>), and Fe<sub>y</sub>N (0.23 mF cm<sup>-2</sup>, 5.75 cm<sup>2</sup>), respectively, suggesting higher density of catalytically active sites exposed in CoNi–Fe<sub>3</sub>N.<sup>[43]</sup> In order to estimate the intrinsic activities of active sites, we normalize the current densities of NTs by

the corresponding relative ECSA (J<sub>ECSA</sub>, Figure S18, Supporting Information). To deliver the  $I_{ECSA}$  of 200  $\mu$ A cm<sup>-2</sup>, CoNi-Fe<sub>3</sub>N, Ni-Fe<sub>3</sub>N, and Co-Fe<sub>3</sub>N require 325.9, 332.6, and 339 mV, respectively, which are lower than that of Fe<sub>v</sub>N (371 mV). The intrinsic activity follows the trend of  $CoNi-Fe_3N > Ni-Fe_3N > Co-Fe_3N > Fe_{\nu}N$ , consistent with that after electrode area normalization, further highlighting the CoNi doping induced improved specific activity. What's more, when deliver  $I_{ECSA}$  below 66  $\mu$ A cm<sup>-2</sup>, the CoNi–Fe<sub>3</sub>N needs slightly larger potential than Ni-Fe<sub>3</sub>N. These results highlight the synergetic advantages of ECSA and intrinsic activity in enhancing catalytic activity of CoNi-Fe<sub>3</sub>N. Moreover, to investigate the possibility of scale-up production, the catalytic activity of NTs with different areas were evaluated. As shown in Figure S19 in the Supporting Information, the LVS plots for NTs with working areas of 0.07, 0.20, and 2.54 cm<sup>2</sup> are overlapped; and the Tafel slopes are similar to all Fe<sub>3</sub>N-based NTs, which signifies that working areas have few effects on the catalytic activity.

Further, by varying the atomic doping ratio of Co to Ni, we took advantage of the synergistic doping effect wherein the surface composition of the Fe<sub>3</sub>N are changed-to tune the electronic structure, which is quantified by OER LSV and Tafel measurements. As revealed in Figure S20 in the Supporting Information, the activity trend of Fe<sub>3</sub>N based electrocatalysts was obtained as follows: CoNi-Fe<sub>3</sub>N > Co<sub>1</sub>Ni<sub>3</sub>-Fe<sub>3</sub>N > Co<sub>3</sub>Ni<sub>1</sub>-Fe<sub>3</sub>N > Ni-Fe<sub>3</sub>N >  $Co-Fe_3N > Fe_vN$ , which suggests that the best catalytic activity is achieved by CoNi co-doping with a ratio of 1:1. Additionally, the OER performances of CoNi-FeO<sub>v</sub> and FeO<sub>v</sub> (before nitridation) were also assessed. As displayed in Figure S21 in the Supporting Information, the  $\eta_{10}$  values of CoNi-FeO<sub>w</sub> Co-FeO<sub>v</sub>, and Ni-FeO<sub>v</sub> are lower than that of FeO<sub>v</sub> by 230–276 mV, further indicating the synergistic effect of three metal atoms in enhancing the OER activity. As expected, CoNi-Fe<sub>3</sub>N demonstrates markedly higher activity than that of CoNi-FeO,, highlighting the importance of metallic feature of Fe<sub>3</sub>N. Furthermore, CoNi-Fe<sub>3</sub>N shows remarkable stability during OER testing. Figure 3g presents the  $\eta$ -t plot for CoNi-Fe<sub>3</sub>N with current density increasing from 10 to 200 mA cm<sup>-2</sup> by four steps. Remarkably, after a series of high current density flowing, once current density is reverted to 10 mA cm<sup>-2</sup>, the voltage promptly resumes. Such well repeated curves suggest fast mass transportation nature of CoNi-Fe<sub>3</sub>N, as well as excellent endurance for quick emigration of drastic gas bubbles. Moreover,  $\eta_{10}$ and  $\eta_{100}$  of CoNi-Fe<sub>3</sub>N increase respectively by only 2.5 and 7.0 mV after 1000 LSV cycles, again proving good durability (inset of Figure 3g). Additionally, according to the suggested benchmark criteria,<sup>[44,45]</sup> the stability of CoNi-Fe<sub>3</sub>N was examined by chronopotentiometry under a current density of 10 mA cm<sup>-2</sup>. As shown in the Figure S22 in the Supporting Information, the potential for RuO2 increases from 1.57 to 1.72 V in 3 h and rises sharply to 2.03 V, losing all its activity. On the contrary, CoNi-Fe<sub>3</sub>N remains essentially stable over 33 h chronopotentiometry, which is competitive among the recently reported catalysts (Table S3, Supporting Information). Furthermore, overall water splitting test was conducted using CoNi-Fe<sub>3</sub>N as anode and Pt/C as cathode (CoNi-Fe<sub>3</sub>N(+)||Pt/C(-)). The CoNi-Fe<sub>3</sub>N(+)||Pt/C(-) drives a current density of 10 mA cm<sup>-2</sup> at 1.59 V, which outperforms Fe<sub>v</sub>N(+)||Pt/C(-) (1.74 V) and RuO<sub>2</sub>(+)||Pt/C(-) (1.65 V) electrolyzers (Figure S23, Supporting Information). These responses demonstrate that  $CoNi-Fe_3N$  can facilitate mass transport and possesses intrinsic robustness for prolonged electrolysis upon oxygen evolution.

## 2.3. Insights Into OER-Conditioned Catalysts

To track the evolution of chemical composition and surface states of catalysts during OER, quasi-in situ XRD and XPS were carried out. As revealed in potential-dependent XRD patterns, the CoNi-Fe<sub>3</sub>N sample exhibits new signals originating from FeOOH (PDF#29-0713) with crystal planes of (140), (041), and (141) along with increasing anodic potential (Figure 4a), indicating distinct phase evolution towards heterostructure of CoNi-FeOOH and CoNi-Fe<sub>3</sub>N. Simultaneously, the XRD intensities of Fe<sub>3</sub>N peaks in CoNi-Fe<sub>3</sub>N are changed accompanied with the generation of CoNi-FeOOH. The evolution of Fe<sub>3</sub>N peaks is depended on the interplanar spacing and atomic packing density of corresponding lattice planes, which can be represented by the texture coefficients  $(TC_{hkl})$  as a function of anodic potential (Supporting Information). As displayed in Figure S24 in the Supporting Information, with increasing anodic potential applied to the CoNi-Fe<sub>3</sub>N catalyst, TC<sub>113</sub> of Fe<sub>3</sub>N enhances, while TC<sub>110</sub>, TC<sub>111</sub>, TC<sub>112</sub>, and TC<sub>002</sub> decrease conversely. Notably, according to Bragg equation and atomic structure of crystal planes (Figure 4b), (113) plane possesses the smallest interplanar spacing (1.24 Å) and most sparse atoms in Fe<sub>3</sub>N crystal; while the other crystal planes with decreased TC values have larger interplanar spacing and higher densely packed atoms than that of (113) plane. Therefore, it can be understood that the Fe<sub>3</sub>N crystal planes with large interplanar spacing (>1.24 Å) and high densely packed atoms tend to subject to the OH- attacking and sequentially enable the transformation into FeOOH during OER,<sup>[46]</sup> resulting in a decreased XRD signal. Similarly, the Co-Fe<sub>3</sub>N and Ni-Fe<sub>3</sub>N demonstrate new XRD peaks for FeOOH under OER condition, as well as the potential-dependent variation of TChkl values for Fe<sub>3</sub>N (Figure S25, Supporting Information), which reveal the same phase transformation from Fe<sub>3</sub>N into FeOOH during OER process. Interestingly, the undoped Fe<sub>v</sub>N sample demonstrates almost the same XRD pattern with the pristine one, indicating the unchanged crystallinity (Figure 4c). These findings confirm the role of CoNi substitution in tuning the kinetics of Fe<sub>3</sub>N surface reconstruction.

Potential-dependent XPS spectra reveal more detailed surface evolution of the electronic structure. As illustrated in the quasi-in situ XPS spectra (Figure 4d),  $Fe^{\delta+}$  peaks in CoNi–Fe<sub>3</sub>N shift negatively by 0.42 eV when the voltage passes from open circuit potential (OCP) to 1.4 V. This shifting is attributed to the accumulation of adsorbed OH<sup>-</sup> ions driven by the anodic potential, which then replaces the N<sup>3-</sup> in the CoNi–Fe<sub>3</sub>N NTs, leading to unsaturated Fe sites with dangling bonds.<sup>[47]</sup> As the OER potential further increases to 1.4 and 1.6 V, Fe<sup> $\delta+$ </sup> peaks shift positively and Fe<sup>0</sup> species disappear entirely, indicating the oxidation of Fe<sub>3</sub>N towards in (oxyhydr)oxides. Simultaneously, Ni<sup> $\delta+$ </sup> (Figure 4e) and Co<sup> $\delta+$ </sup> (Figure 4f) in CoNi–Fe<sub>3</sub>N demonstrate similar evolution with increasing anodic potential, indicating the similar chemical environment of Ni and Co cations with Fe. Thus, the trimetallic sites all participate in the phase transformation. In addition, the Co(0) and Ni(0) exist under entire potential range, which may be attributed to the stable Co and Ni species inside NTs. Compared with the catalysts at OCP, Fe  $2p_{3/2}$  peak at 1.6 V shifts negatively, which implies more Fe atoms with dangling bonds are existed after the oxidation of CoNi-Fe<sub>3</sub>N toward oxyhydroxide.<sup>[47]</sup> The Fe atoms with dangling bonds should be generated along with the OH adsorption and desorption on oxyhydroxide. Different from the Fe atoms, the 2p<sub>3/2</sub> peaks of Co and Ni at 1.6 V shift positively compared with the one at OCP, signifying much stronger affinity of Fe site to OH species than Co and Ni in CoNi-FeOOH, consistent with the finding of previous work<sup>[48]</sup> as well as the small  $\Delta G_{*OH}$  of Fe site in DFT calculations section below. Concurrently, the intensity of N 1s under OER is weaker than that of pristine states, which is ascribed to the replacing of  $N^{3-}$  with  $OH^{-}$  (Figure S26, Supporting Information).<sup>[3,49]</sup> Such chemical bonds evolution can also be reflected by the potential-dependent changes of O-M and O-H contents in the O 1s XPS spectra (Figure 4g and Table S4, Supporting Information). At 1.2 V, CoNi-Fe<sub>3</sub>N NTs display OH<sup>-</sup> accumulation on surface, which indicates the orbital hybridization between metal atoms in NTs and O atoms in OH<sup>-,[50]</sup> manifesting the generation of CoNi-Fe(OH)<sub>r</sub>. As potential steps to 1.4 V, NTs show further increased O-M content and decreased O-H content, suggesting the reconstruction towards oxyhydroxides. Conversely, pure Fe<sub>v</sub>N without CoNi doping requires a higher anodic potential of 1.4 V for adsorbing OH<sup>-</sup> species; and it shows minimum changes to oxyhydroxides even at 1.6 V. The significant different behaviors highlight the essential role of CoNi co-doping in modulating the electronic structure of Fe<sub>3</sub>N and facilitating bond reconstruction.

To inspect the surface reconstruction more intuitively, SEM and TEM of OER-conditioned CoNi-Fe<sub>3</sub>N NTs were further conducted. Comparing with pristine catalyst (Figure 5a), the surface of CoNi-Fe<sub>3</sub>N NTs become obviously rougher, when the potential steps to 1.2 V (Figure 5b). Further increasing the potential to 1.4 V, the nanoparticles in NTs wall evolve into refined grains (Figure S27, Supporting Information), while the primary array skeletons are still preserved, forming connected nanopillars with abundant mesopores (Figure 5c). These obvious changes indicate that the induced bond reconstruction by the OER catalysis concomitantly alters the morphology of CoNi-Fe<sub>3</sub>N. Notably, as revealed in Figure S28 in the Supporting Information, the CoNi-Fe<sub>3</sub>N NTs composed of refined nanoparticles are still arranged in regular array after OER stability test, no aggregation of tubes is observed, which indicates the robustness of NTs wall for high potential and even for longterm catalysis. The in situ formed fluffy species on surface offer more homogeneous multi-metal sites on surface and provides a larger fraction of electrolyte-permeable catalyst participating in catalysis. In situ HAADF-STEM images (Figure S29, Supporting Information) also reveal the nanoparticle refinement under operando OER condition. Furthermore, as demonstrated in the real-time SAED patterns, besides the primitive dotted rings from pristine Fe<sub>3</sub>N at OCP (Figure 5d), a diffuse set of concentric rings corresponding to Fe(OH)<sub>3</sub> (PDF#46-1436) are emerged when the applied potential rises to 1.2 V (Figure 5e), which further transforms into FeOOH with polycrystalline structure at 1.4V (Figure 5f). This potential-dependent crystal structure evolution indicates that the surface of CoNi-Fe<sub>3</sub>N







**Figure 4.** In situ probing of OER-conditioned CoNi–Fe<sub>3</sub>N NTs. a) Potential-dependent XRD patterns of CoNi–Fe<sub>3</sub>N NTs. b) Crystal structures of various Fe<sub>3</sub>N crystal planes. c) XRD patterns of pristine and post-OER Fe<sub>9</sub>N NTs. Potential-induced XPS spectra of d) Fe  $2p_{3/2}$ , e) Ni  $2p_{3/2}$ , and f) Co  $2p_{3/2}$  for CoNi–Fe<sub>3</sub>N. g) OER LSV plots of Fe<sub>9</sub>N and CoNi–Fe<sub>3</sub>N. Insets of (g): corresponding XPS spectra of O Is under OCP, 1.2, 1.4, and 1.6 V.

partially reconstructs into CoNi–FeOOH via CoNi–Fe(OH) $_3$  during OER catalysis, which is consistent with our previous OER-conditioned XRD and XPS analyses.

The potential-dependent HRTEM and corresponding fast Fourier transform (FFT) images further display the detailed lattice reconstruction of CoNi–Fe<sub>3</sub>N during OER. With the stimulation of the potential pulse, well-crystallized Fe<sub>3</sub>N lattice fringes in CoNi–Fe<sub>3</sub>N (Figure 5g) convert into mixture domains with orthorhombic Fe(OH)<sub>3</sub> and hexagonal Fe<sub>3</sub>N at the edge of NTs (Figure 5h). Following, the orthorhombic Fe(OH)<sub>3</sub> transforms into orthorhombic FeOOH (Figure 5i). In addition, HRTEM and FFT images also display a small fraction







Figure 5. Morphology and phase evolution OER-conditioned CoNi–Fe<sub>3</sub>N NTs. SEM and TEM images of CoNi–Fe<sub>3</sub>N NTs at a) OCP, b) 1.2 V, and c) 1.4 V. d–f) In situ SAED patterns of CoNi–Fe<sub>3</sub>N during catalysis. g–i) In situ HRTEM image (top) and FFT patterns (bottom) of the CoNi–Fe<sub>3</sub>N during catalysis.

regions with no lattice fringes under OER, which indicates that surface amorphization of CoNi–Fe<sub>3</sub>N is accompanied by the formation of irregular CoNi–Fe(OH)<sub>3</sub> and CoNi–FeOOH nanodomains. These bond, morphology, and lattice evolutions collectively reveal the phase reconstruction of CoNi–Fe<sub>3</sub>N towards CoNi–FeOOH via CoNi–Fe(OH)<sub>3</sub> intermediate during the OER process. The synergistic effect of inner CoNi–Fe<sub>3</sub>N matrix and external CoNi–FeOOH greatly accelerates the catalytic kinetics, and in situ formed CoNi–FeOOH on the CoNi–Fe<sub>3</sub>N

surface should be the genuine intrinsic active species toward OER catalysis. These in situ formed heterostructure renders a close interconnection between the parent metallic CoNi–Fe<sub>3</sub>N and the newly generated CoNi–FeOOH, ensuring the excellent conductivity. Similar surface amorphization is also observed in some 3d metal-based compounds, such as  $Co_{1-x}Ni_xS_2$ ,<sup>[8]</sup> NiFe Prussian blue analogues,<sup>[5]</sup> and Fe(PO<sub>3</sub>)<sub>2</sub>,<sup>[13]</sup> respectively (Table S5, Supporting Information). Unlike those amorphous (oxyhyr)oxides, crystalline CoNi–FeOOH is evidenced in the

post-OER CoNi–Fe<sub>3</sub>N, which confirms that CoNi co-incorporation is favorable for the orderly rearrangement of Fe atoms in Fe<sub>3</sub>N toward FeOOH. More importantly, compared with the common Fe/Co/Ni layered double hydroxides  $(LDH)^{[51]}$  and oxides,<sup>[52]</sup> which can also undergo reconstruction during OER, the metallic CoNi–Fe<sub>3</sub>N can ensure the electronic conductivity for generated CoNi–FeOOH, which is highly important for efficient electrocatalysis.

To compare the catalytic performances of the conventional and transformed oxyhydroxides, we further prepared the routine CoNi–FeOOH (*r*-CoNi–FeOOH) control sample through a solution chemical route. As illustrated in Figure S30 in the Supporting Information, *r*-CoNi–FeOOH displays  $\eta_{10}$  and Tafel slope of 353 mV and 47 mV dec<sup>-1</sup>, underperforming the CoNi– Fe<sub>3</sub>N (285 mV and 34 mV dec<sup>-1</sup>) here. This result confirms that the synergistic advantage of the surface-reconstructed CoNi–FeOOH and the metallic CoNi–Fe<sub>3</sub>N core for enhancing the catalytic activity. Indispensably, the CoNi incorporation in CoNi–Fe<sub>3</sub>N catalyst exerts a fundamental role in guaranteeing the generation of active oxyhydroxides layer as well as the high catalytic efficiency.

#### 2.4. DFT Calculations

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We conducted DFT calculations aiming at simulating the structural reconstruction of CoNi-Fe<sub>3</sub>N during OER catalysis. According to the OER-conditioned XRD patterns, the intensity of Fe<sub>3</sub>N peaks in pristine CoNi-Fe<sub>3</sub>N changes along with the reconstruction towards CoNi-FeOOH during catalysis. This means that the process of CoNi-Fe<sub>3</sub>N reconstruction can be simulated by investigated on Fe<sub>3</sub>N crystal structure. Fe<sub>3</sub>N surface with varying hydroxyl coverage (0.25 to 1.25 monomolecular layer (ML)) was investigated to simulate the adsorption process of OH species (Figure S31, Supporting Information). When the surface coverage is in the range of 0.25-1.0 ML (top of Figure 6a), OH species are adsorbed on the bridging Fe-Fe sites, exhibiting the characteristics of Fe(OH)<sub>3</sub> crystal (Figure S32, Supporting Information). Further increasing the surface coverage to 1.25 ML, adsorbed OH starts to dissociate in between the Fe atoms and lose the H atom, generating the Fe-O-Fe motif that shows the structural characteristics of FeOOH crystal. Thus, Fe<sub>3</sub>N can be converted into Fe(OH)<sub>3</sub> and even FeOOH through increasing OH coverage, exactly reproducing the structural evolution experimentally observed in CoNi-Fe<sub>3</sub>N NTs. Noticeably, when introducing lattice distortion into Fe<sub>3</sub>N (i.e., Fe vacancies (V<sub>Fe</sub>), Figure S33, Supporting Information), Fe-O-Fe motifs representing for FeOOH are generated with a less surface coverage (0.75 ML, bottom of Figure 6a), and the OH adsorption is facilitated with a more negative energy ( $E_{ads}$ , -1.14 eV) than that of pristine Fe<sub>3</sub>N (-0.95 eV, Figure S34, Supporting Information). It reveals a stronger OH adsorption and promoted phase transition on Fe<sub>3</sub>N with lattice distortion. Furthermore, as revealed in the projected density of states for Fe 3d (PDOS, Figure 6b), d-band center ( $\varepsilon_d$ ) of Fe atoms in Fe<sub>3</sub>N upshifts towards Fermi level ( $\varepsilon_{\rm f}$ ) after CoNi co-incorporation. The upshifted d-band center increases the content of empty antibonding states above  $\varepsilon_{f}$ , which endows Fe centers with stronger affinity for OH species,<sup>[28,47]</sup> and thus

promotes the surface reconstruction towards oxyhydroxides. These results are consistent with the in situ experimental results as shown in Figures 4 and 5.

Computational studies were further used to rationalize the improved OER performance and identify the catalytic active site. Due to the surface reconstruction during OER, CoNi co-doped active FeOOH (CoNi–FeOOH) and single metal doped FeOOH (Co–FeOOH and Ni–FeOOH), as well as bare FeOOH were optimized to identify the effect on modulating OER energetics (Supporting Information). As outlined in Figure 6c, Gibbs free energies of each step during OER (Equations (1)–(4),  $\Delta G_{1-4}$ ) were calculated on different metal sites to obtain the energy profiles along OER pathway (Table S6, Supporting Information).

As depicted in Figure 6d, Gibbs free energy for first hydroxyl filling process on FeOOH is 0.38 eV ( $\Delta G_1$ ), demonstrating an overstrong adsorption of OH on FeOOH surface. As a consequence, subsequent formation of \*O and \*OOH would encounter larger potential barrier (Figure S35, Supporting Information). The activity of the single-site doped Co-FeOOH and Ni-FeOOH was then assessed (Figures S36 and S37, Supporting Information). In Co-FeOOH, the Fe atom exhibits the  $\Delta G_1$  of 0.48 eV, indicating still too strong adsorption of OH; while, Co site displays over weak adsorption of OH  $(\Delta G_1 = 2.122 \text{ eV})$ , which extremely suppresses the OER process on Co-FeOOH. By adding Ni into FeOOH, Fe atom displays increased \*OH formation energetics of 0.823 eV, effectively alleviating the strong adsorption of OH on FeOOH. As for CoNi codoped FeOOH, Fe and Co sites demonstrate relatively moderate adsorption of OH with  $\Delta G_1$  of 0.92 and 1.068 eV, respectively, but still far away from the optimal value of 1.23 eV (Figure S38, Supporting Information). Notably, the Ni site of CoNi-FeOOH exhibits near-optimal \*OH energetics ( $\Delta G_1 = 1.305$  eV) for OER, which should contribute to a high activity.

Energetics of all intermediates (\*OH, \*O, and \*OOH) were further calculated to extract the critical minimum overpotential  $(\eta_{cal})$  required for all OER elementary steps. The free energies for \*OH and \*OOH intermediates have a good linear scaling relationship of  $\Delta G_{*OOH} = 0.61 \Delta G_{*OH} + 3.2 \pm 0.2$  eV (Figure 6e), similar to previous reports.<sup>[33,34]</sup> Based on this and taking the competition between free energies of the four steps into consideration, a 2D map of OER activity ( $\eta_{cal}$ ) is constructed with respect to \*O and \*OH energies (Figure 6f). As expected, too strong interaction of OH on FeOOH surface (lower  $\Delta G_{*OH}$ ) is detrimental for the subsequent steps, leading to  $\eta_{\rm cal}$  of 347 mV. After single-site doping, Co-FeOOH exhibits high  $\Delta G_{*O} - \Delta G_{*OH}$  (1.840 eV), causing large  $\eta_{cal}$  of 610 mV, which suppresses the activity of FeOOH. While Ni atom doping results in moderate regulation in both  $\Delta G_{*OH}$  and  $\Delta G_{*O}$  –  $\Delta G_{*OH}$ , making Ni–FeOOH more active ( $\eta_{cal} = 332$  mV) than FeOOH and Co-FeOOH. Of note, CoNi-FeOOH demonstrates the best OER activity with  $\eta_{\rm cal}$  of 265 mV, close to the summit of OER volcano plot. In general,  $\eta_{\rm cal}$  follows the same trend with the experimental values ( $\eta_{10,exp}$ ) on reconstruction-derived catalysts: CoNi-FeOOH (CoNi-Fe<sub>3</sub>N) > Ni-FeOOH (Ni-Fe<sub>3</sub>N) > Co-FeOOH (Co-Fe<sub>3</sub>N) (Figure 6g). Combining experiments and DFT calculation results, the enhanced activity of CoNi-Fe<sub>3</sub>N, Ni-Fe<sub>3</sub>N, and Co-Fe<sub>3</sub>N is attributed to the facilitated generation of active oxyhydroxides. While the activity difference ADVANCED SCIENCE NEWS \_\_\_\_\_ www.small-journal.com



**Figure 6.** Theoretical calculations. a) Simulated structural reconstruction process from Fe<sub>3</sub>N to FeOOH with increasing of OH coverage (0, 0.25, 0.50, 0.75, 1.0, and 1.25 ML). b) Calculated PDOS on d-orbital of Fe atoms in Fe<sub>3</sub>N and CoNi–Fe<sub>3</sub>N. c) OER pathway on CoNi–FeOOH catalyst. d) Calculated free energy diagram for OER on the metal active sites (M) of FeOOH ([Fe]\_M), Co–FeOOH ([Co–Fe]\_M), Ni–FeOOH ([Ni–Fe]\_M), and CoNi–FeOOH ([CoNi–Fe]\_M) catalysts. e) Linear relation between  $\Delta G_{*OH}$  and  $\Delta G_{*OOH}$ . f) OER activity volcano plots of  $\eta_{cal}$  as a function of Gibbs free energies of the reaction intermediates. g) Comparison of  $\eta_{cal}$  and  $\eta_{10,exp}$  values.

of bimetallic (Co–FeOOH and Ni–FeOOH) and trimetallic (CoNi–FeOOH) catalysts can be ascribed to the different adsorption energies of oxygenated intermediates on active sites.

Ni doping can enhance the activity of Fe site by optimizing the energetics of \*OH, which results the higher activity of Ni–Fe<sub>3</sub>N than that of Co–Fe<sub>3</sub>N. In bimetallic Co–FeOOH and Ni–FeOOH

catalysts, the Fe atoms are identified as active site, which is agree with previous reports.<sup>[53,54]</sup> Fe site of reconstructed trime tallic CoNi–FeOOH also demonstrates improved activity than FeOOH. But more importantly, the Ni site in CoNi–FeOOH exhibits more optimal activity than Co and Fe sites, which is the actual active site and responsible for the high activity of trime-tallic catalyst.

## 3. Conclusion

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In summary, CoNi co-incorporated Fe<sub>3</sub>N NTs are fabricated on the iron foil through an anodization/electrodeposition/nitridation process for use of the OER catalysis. CoNi-Fe<sub>3</sub>N undergoes a surface structural change with electrochemical treatment, and demonstrates high OER catalytic activity and remarkable stability in alkaline electrolyte. Potential-dependent results as well as DFT simulations reveal that CoNi doping induces structural distortion and up-shift d-band center in Fe<sub>3</sub>N, facilitating the OH adsorption and consequently the surface reconstruction of CoNi-Fe<sub>3</sub>N NTs into crystalline CoNi-FeOOH as active species. As a result, CoNi-Fe<sub>3</sub>N NTs exhibit a supreme OER catalytic activity over undoped Fe<sub>v</sub>N NTs or single-metal doped Co-Fe<sub>3</sub>N and Ni-Fe<sub>3</sub>N NTs. Moreover, the Ni atom is proved to be genuine OER catalytic active site in CoNi-FeOOH, accounting for the excellent catalytic performance of CoNi-Fe<sub>3</sub>N NTs. These findings would supply a new insight into developing high-efficient OER catalysts through adjusting dynamic self-reconstruction.

### 4. Experimental Section

Materials Synthesis: Firstly, FeO, films were obtained by anodizing iron foil (0.1 mm thick, 99.999%, Alfa Aesar) at 50 V for 40 min. The electrolyte is an ethylene glycol solution containing 0.1 м NH<sub>4</sub>F (Sigma-Aldrich) and 1.0 M water. Subsequently, Ni and Co were introduced into FeO<sub>v</sub> to obtain CoNi–FeO<sub>v</sub> by electrodepositing in an aqueous solution containing NiCl<sub>2</sub>  $(0.09 \text{ mol } L^{-1})$ , NiSO<sub>4</sub>  $(0.46 \text{ mol } L^{-1})$ , CoCl<sub>2</sub>  $(0.10 \text{ mol } L^{-1})$ , and CoSO<sub>4</sub> (0.48 mol L<sup>-1</sup>, Sinopharm Chemical Reagent Co., Ltd.) with a pH value of 2.5 tuned by boric acid (Fisher Scientific). The anodization and deposition were conducted on a direct-current (DC) supply (HSPY-60-05). The deposition process was performed in two-electrode electrolytic cell with a Pt counter electrode at 25 °C. After that, CoNi–FeO<sub>y</sub> films were annealed at 400 °C for 1 h in an atmosphere composed of argon (200 sccm) and NH<sub>3</sub> (100 sccm) at 3.0 Torr to produce CoNi-Fe<sub>3</sub>N NTs. The Fe<sub>3</sub>N NTs doped with different molar ratios of Co and Ni were also prepared by simply changing concentration of electrolyte solution while keeping other conditions identical. The Fe<sub>3</sub>N NTs doped with Co and Ni with a molar ratio of 1:1 denoted as CoNi-Fe<sub>3</sub>N. As a control, Co-Fe<sub>3</sub>N and Ni-Fe<sub>3</sub>N NTs, together with  $Fe_{\nu}N$  NTs were prepared for comparison. Co-Fe<sub>3</sub>N was prepared without NiCl<sub>2</sub> and NiSO<sub>4</sub>, Ni-Fe<sub>3</sub>N was prepared without CoCl<sub>2</sub> and CoSO<sub>4</sub>, and Fe<sub>v</sub>N NTs were prepared without electrodeposition by the same procedures of CoNi-Fe<sub>3</sub>N NTs. Routine FeOOH (r-FeOOH) was synthesized by heating 0.5 mmol FeSO<sub>4</sub>, 1 mmol CH<sub>3</sub>COONa, and 20 mL of water at 100 °C for 8 h, in the Teflon-lined autoclave. The r-CoNi-FeOOH was prepared by doping Co and Ni into FeOOH through the same electrodeposition process of CoNi-Fe<sub>3</sub>N.

Materials Characterization: Morphology of samples was investigated by JEOL-JSM-7001F SEM, JEOL-JEM-2100F TEM and Cs-corrected Titan G2 (300 kV) electron microscopes. XRD patterns were obtained using a Bruker D8 Advance X-ray diffractometer with GADDS (2D detector) configured with a Co-K $\alpha$  radiation source at 40 kV voltage and 30 mA current, with a scan rate of 0.1° s<sup>-1</sup>. XPS measurements were performed on Thermo-Fisher Scientific ESCALAB 250XI electron spectrometer with Mg K $\alpha$  nonmonochromated flood source (400 W, 75 eV pass energy). ICP–MS data were obtained by NexION 350 instrument. Water and airbubble CA were recorded using DSA100 contact angle analyzer (Kruss, Germany). The mass loading of films on iron foil is  $\approx$ 0.92 mg cm<sup>-2</sup>, which was measured on EX225ZH/AD electronic balance.

Electrochemical Measurements: Electrochemical characterizations were carried out on a CHI 760e electrochemical workstation (Chenhua, Shanghai). OER activity was evaluated in a three-electrode system with Pt wire (CHI 115) as counter electrode, NTs on iron foil as working electrodes, and Hg/HgO as reference electrode in 1.0 м KOH electrolyte. During the measurement, high-purity  $O_2$  was bubbled through the electrolyte to saturate it and fix the reversible oxygen potential. LSV was performed at scanning rate of 5 mV s<sup>-1</sup>. An ohmic drop iR correction was applied to compensate potential losses resulting from the resistance of the electrolyte solution. To analyze the redox processes, the CV curves were tested with larger scan rate of 10 mV  $s^{-1}$  at potential range of 0.9 to 1.55 V versus RHE. Commercial RuO<sub>2</sub> (76%) and Pt/C (20%, Johnson Matthey) ink was prepared by dispersing 5 mg sample in 500 µL solvent containing 25 μL of water, 450 μL of ethanol and 25 μL Nafion solution (Alfa Aesar) and then sonicating for 2 h. The ink loaded onto iron foil with optimal loading density of 1.25 mg cm<sup>-2</sup> was measured as benchmark OER and HER catalyst.<sup>[12]</sup> In situ EIS was carried out on a Solartron analytical 1287A potentiostat/galvanostat coupled with a 1260A Frequency Response Analyzer (FRA) (England). EIS spectra was collected in potential range from 1.18–1.63 V by applying different dc potentials covering the frequency range from 0.01 to 100 kHz. Sinusoidal amplitude of 5 mV was applied throughout the tests to ensure linear response of the electrode.

Theoretical Calculations: DFT were carried out using Perdew–Bruke– Emzerhof (PBE) exchange correlation functional and the soft projector augmented wave (PAW) pseudopotential, as implemented in the Vienna AB Initio Simulation Package (VASP) program. The energy cutoff and *k*-point Gamma-centered grid was set to 500 eV and  $2 \times 2 \times 1$  Monkhorstpack *k*-point mesh, respectively. All structures were optimized until the forces on each ion were less than 0.02 eV Å<sup>-1</sup>, and the convergence criterion for the energy was 10<sup>-4</sup> eV.

# **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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## **Conflict of Interest**

The authors declare no conflict of interest.

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